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TECHNICAT REPORT NUMBER 7

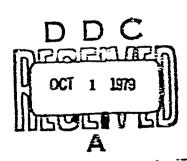
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DEPARTMENT OF THE NAVY OFFICE OF NAVAL RESEARCH METALLURGY PROGRAM - CODE 471

PREPARED BY:

R. THIBEAU, C. BROWN, A. GOLDFARB AND R. HEIDERSBACH DEPARTMENT OF OCEAN ENGINEERING UNIVERSITY OF RHODE ISLAND KINGSTON, RHODE ISLAND 02881



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20. Abstract (cont.)

did not predict the formation of PbO under any conditions; however, spectra indicated the presence of the oxide at certain potentials in acid and neutral solutions and at all potentials above the immunity region in basic solutions. Spectroscopic identification of insoluble surface species was in agreement with potentiodynamic polarization curves.

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INTRODUCTION

Laser Raran spectroscopy can unambiguously identify the compounds present in aqueous corrosion product films on metal surfaces. It can be used to analyze insoluble surface layers in situ without removing a metal sample from the corrosive solution with which it is reacting (1-3). The ability to identify surface species without changing the environment makes this technique ideal for experimental confirmation of theoretical Pourbaix diagrams, which identify the lowest energy species for any given set of conditions.

In situ Raman spectroscopy, in combination with the complementary technique, reflection-absorption infrared spectroscopy, has been used to study the Pourbaix diagrams for the Pb-H₂O and Pb-H₂O-Cl systems (1,2). Potentiostatic exposures of lead electrodes were conducted in buffer solutions and the resulting surface films were analyzed spectroscopically. The compounds comprising the surface corrosion product films were only in partial agreement with Pourbaix diagram predictions. In the present research simple, unbuffered solutions were used for electrochemical exposures to find if experimental results would be closer to those predicted by thermodynamics if the solutions did not contain the extra dissolved species of the buffer systems used previously.

The behavior of lead in sulfate solutions has been studied extensively due to the widespread use of lead-acid storage batteries. For this reason, the preponderance of experimental work has involved the reactions of lead with sulfuric acid, and very little research on lead in neutral or basic sulfate solutions

has been conducted. Pourbaix diagrams for lead in aqueous sulfate solutions have been calculated (4-6). Some efforts have been made to verify the theoretical predictions experimentally, although experimental sulfate exposures have been confined to the acid and neutral regions of the diagram (4,7). The present report describes infrared and Raman spectroscopic results from systematic exposure of lead samples in 6.1 % sulfate solutions under conditions covering a large part of the Pourbaix diagram.

EXPERIMENTAL

Raman spectra were recorded with a Spex Industries Model 1401 double monochromator using a photon counting detection system. A Coherent Radiation Laboratories Model CR-3 argon ion laser was used as the excitation source. Both the 488.0 and 514.5 nm wavelength laser lines were used, and the power at the sample was approximately 500 mm.

Infrared reflection-absorption spectra were obtained with a Wilks Scientific Corporation Model 9 multiple specular reflection attachment in both the sample and reference beams of Perkin-Elmer Model 521 infrared spectrophotometer equipped with a grating polarizer. Details of the special electrochemical cell and instrumentation used for controlled potential sample exposures are contained in a previous report (1).

Lead foil (1.6 mm thick) supplied by Alfa Products. Inc., at greater than 99% purity was used for this investigation. It was cut into 2.8 x 5.7 cm rectangles to fit the sample holder of the electrochemical cell. This size was also required for the infrared reflection attachment. Prior to placing a lead

sample in solution, it was immersed in warm, concentrated ammonium acetate solution for 5 minutes to dissolve the surface layer, leaving a clean, silvery sample. The clean lead sample was washed with distilled water and immediately placed in the exposure solution.

The three solutions used were made from reagent grade compounds. The acid solution was 0.1 M $\rm H_2SO_4$. The neutral solution chosen was 0.1 M $\rm K_2SO_4$ which has a pH of approximately 6.5, and for exposure in basic solution, a solution of 0.1 M $\rm K_2SO_4$ and 0.004 M KOH, giving an approximate pH of 11, was used.

The electrochemical cell filled with solution was pursed with dry nitrogen for 30 minutes before and throughout the controlled potential exposures. The potential of the lead working electrode was held constant relative to the saturated calomel reference electrode by a Wenking Model IT73 potenticistat for ceriods ranging from 1/4 to 21 hours. Upon completion of an exposure period, an in situ Raman spectrum was recorded. The sample was then resolved from the cell, washed thoroughly with distilled water, and allowed to dry in air. The dry sample was returned to the Raman spectrometer for examination and then analyzed by the infrared spectrometers.

Some exposures were conducted on lead films which were vapor deposited onto sold substrates on class microscope slides. These samples allowed the lead to be sompletely oxidized leaving a non-reacted gold mirror substrate. The thickness of oxidized lead films on such samples was measured by a Taylstep-1 stylus type profile instrument.

RESULTS AND DISCUSSION

The Pourbaix diagram for the lead-water-sulface system was calculated using the relationships used by Ruetschi and Angstadt (4) but employing more recent values for the free energy of formation of some species (8). The newer thermodynamic data, summarized in Table I, caused only small changes in the positions of the PbO-PbSO₄ equilibria lines. A sulfate ion activity of 0.1 was used for the calculations resulting in the Pourbaix diagram shown in Figure 1.

Electrochemical exposures were carried out in solutions of the desired pH which were 0.1 molar in sulfate. The solutions used gave pH values of approximately 1, 6.5, and 11 to allow observation of the reactions of lead over a wide portion of the Pourbaix diagram. Measurement of solution pH before and after potentiostatic exposures showed that the pH remained fairly constant, i.e., it did not change by more than 0.5 after as long as twenty-four hours.

In order to provide an experimental basis for choosing exposure potentials, potenticdynamic polarization curves were recorded for lead in the three solutions selected for exposures. Polarization curves were recorded with a relatively slowly changing potential of 40 mV/min to allow the formation of a relatively thick oxidation product film, as would be encountered in potentiostatic oxidation.

The polarization curves are shown in Figure 2. They are rather similar, each has a strong wave at approximately -0.25 V (vs. NHE) as its major feature. These waves mark the transition

from reduction to oxidation, i.e., the upper limit of the immunity region. In accordance with the Pourbaix diagram, the potential of such a transition decreases as pR increases. The oxidative wave was observed at -0.23 V in pH 1, -0.27 V in pH 6.5, and -0.30 V in pH 11 solution. The positions of these waves are in general agreement with the Pb to PbSO₄ and Pb to PbO-PbSO₄ transitions of the Pourbaix diagram.

Potentials used for lead exposures were chosen so that at least one was located in each region of the theoretical Pourbaix diagram and in all potential regions where the polarization curves indicated the possible formation of different species. The exposure conditions selected and the resulting spectra obtained from these potentioscatic exidations are summarized in Table II. pH 1 Exposures: In the 0.1 ft H., SO, solutions used to attain a cldic conditions, lead is stable at low potentials, but it is oxidized to lead sulfate at higher pomentials (4,9,10). After formation of a surface sulfate film thick enough to winder reactions of lead with solution species, layers of PbO or basic lead sulfates develop under the sulfate film at potentials of +0.32 V and higher (4,9,11). Although the formation of underlying oxide layers was not considered in the calculation of the Pourbair diagram, the very weak wave at +0.34 V _.. the nf l polarization curve may indicate the commencement of formation of another compound beneath the sulfate film.

Potentiostatic exposures of lead in 0.1 M sulfuric acid formed surface files whose compositions agreed well with X-ray diffraction work by Pavlov and Tordanov (11). Raman and infrared spectro-

scopic results indicate three ranges of potential: immunity, lead sulfate, and a lead sulfate-lead monoxide region.

At potentials below -0.2; V, ead appeared to be immune to oxidation. An insoluble surface layer was not detected by in situ Raman spectroscopy, samples remained clean and shiny, and current flow was in the reducing direction. When samples exposed in this region were washed and allowed to dry, a nonuniform, light gray surface coating appeared. Infrared spectra lintified the surface layer composition as lead sulfate and orthohombic PbO. Raman spectra of dry sample surfaces confirmed this finding but showed that the sulfate and oxide were not found together but were occupying separate parts of the sample surface. The appearance of these compounds probably results from precipitation of dissolved lead compounds after removal of the applied potential (2). In the generally reducing conditions of this region, it is unlikely that any lead would be directly oxidized at the electrode surface during the potentiostatic exposure. The formation of PbO and lead sulfate is probably a result of the sample removal, washing, and drying process.

At potentials higher than the -0.23 V wave of the polarization curve, net current flow was in the oxidizing direction and spectra showed that lead sulfate was formed. Oxidation at -0.26 V and -0.02 V resulted in PbSO₂ films.

Exposure at potentials higher than the wave at $\pm 0.34 \, \mathrm{V}$ gave surface films identified as tetragonal PbO and PbSO₄, in agreement with the findings of earlier research (11,12). A Raman spectrum of the film in this potential region is compared with one of a

purely PbSO₄ film and with the spectrum of reagent grade PbSO₄ powder in Pigure 3.

Although it was not possible to measure the relative amounts of PhO and PbSO, in the surface films from their spectra, just as it is impossible to measure film thickness, observation of strong tetragonal PbO spectra gave ar indication of the thickness of films analyzed by these techniques. Ruetschi (9) developed a model for the PbO/PbSO, two phase film formed by oxidation of lead in sulfuric acid solutions. He assumed that a surface film with a thickness on the order of a micron was needed before any underlying tetragonal PbO could form (4). Electrochemical measurements and calculations based on ion diffusivity in the films determined that a 24 hour exposure of lead in 4.2 M H2SO4 in the range of +0.2 to +1.1 V would give a film consisting of one mirron of lead sulfate covering one micron of tetragonal PDO. The ability to record strong spectra of the underlying layer of PbO gives indication that Raman and infrared spectroscopy can examine the entirety of films with thicknesses on the order of a micron. pH 6.5 Exposures: The lead-water-sulfate Pourbaix diagram predicts that in a pH 6.5, 0.1 M sulfate solution lead should be stable at potentials below -0.3V, PbO, should form above +0.9 V, and PbSO, should be found at potentials in between. The lower transition was observed in the polarization curve for lead in the 3.1 M $\rm K_2SO_4$ solution used, but the transition to $\rm PbO_2$ was not observed. The polarization curve shows a weak wave at +0.06 V which does not correspond to any feature of the Pourbaix diagram.

Potentiostatic exposures resulted in films with compositions which were in better agreement with the polarization curve than

with the Pourbaix diagram. Exposure at potentials below the -0.27 V wave resulted in immunity. Current flow was in the reducing direction, the surface remained clear and shiny, and no spectra were obtained in so'ution or in air. Higher potentials resulted in oxidation of the lead electrode and formation of insoluble surface files. Files consisted of lead sulfate up to -0.24 V and, above that, tetragonal PbC covered the sample surfaces.

The formation of lead sulfate was in agreement with the Pourbaix diagram, but the PbSO₄ gave slightly different spectra from the sulfates examined previously. As shown in Figure 4, the sulfate film gave an exceptionally strong 451 cm⁻¹ Raman band, the band associated with the 0-S-0 bending vibration (13). Infrared reflection spectra also had a sharp band at 451 cm⁻¹ as shown in Figure 5. Such a vibration is not infrared active in normal sulfate compounds. The unusual intensity of the 451 cm⁻¹ band is assumed to be due to a distortion of the normal lead sulfate lattice.

The broad wave at <0.06 V is near the potential where film composition changed from lead sulfate to tetragonal PbC, and it may be due to such a transition. Lead morexide films were black in color and gave no evidence of the presence of sulfate. The transition from sulfate to PbO was not considered in calculating the Pourbaix diagram, since this reaction was not anticipated. No waves were observed at higher potentials and spectra did not indicate a change to the PbO₂ predicted by the Pourbaix diagram.

pH 11 Exposures: oxidation of lead at a pH of 11 was predicted to form a basic lead sulfate, PbO-PbSO₄, at potentials between -6.45 V and +0.50 V and PbO₂ at higher potentials. The solution used, 0.1 M M₂SO₄ with enough KOH added to make the initial pH 11, resulted in a polarization curve with only one clear oxidation feature. The experimentally observed wave, or group of waves, at approximately -0.30 V represents the transition from lead stability to the formation of an oxidized species. The oxidative change seen above +0.80 V in Figure 2 could represent a transition to a higher oxidation state, but it is probably due to the decomposition of water to evolve oxygen.

Potentiostatic exposures were conducted throughout the potential range where water is stable. As expected, exposure at low potentials gave extremely low current flow in the reducing direction, and no Raman bands were observed. Lead is immune to oxidation below the -0.30 Y wave of the polarization curve.

All exposures at higher potentials resulted in the formation of tetragonal PbO surface films. An oxidation at -0.34 V, a potential higher than the first lobe of the oxidative wave, resulted in a film which gave a strong tetragonal PbO spectrum. Although the wave at -0.30 V seems to be made up of three separate waves, all exposures at potentials above -0.45 V, where the current recorded in the polarization curve first became oxidative, formed tetragonal PbO.

Although the composition of the films was identified as PDO, Raman spectra recorded in solution were somewhat misleading. In situ spectra, as shown in Figure 6, contained the strong bands of tetragonal PtO but also the 980 cm⁻¹ band characteristic of

the SO4 symmetric stretching vibration and a broad band in the 450 cm⁻¹ ragion. Except for the broadness of the 450 cm⁻¹ band, these spectra took like a mixture of PbO and PbSO₄. Upon wishing the samples thoroughly, however, those bands characteristic of sulfate disappeared. Dry sample spectra indicated only tetragonal PbO. The sulfate bands, which can be distinguished from those of PbSO₄ by the broad 450 cm⁻¹ band (lead sulfate has two sharp bands in that region, at 439 and 451 cm⁻¹), are due the sulfate of the solution. The bulk sulfate solution cave the same sulfate spectrum. The change in the spectrum caused by washing the samples was evidence that spectra of both wet and dry samples are needed to distinguish solution or adsorbed species from those compounds which were actually part of an insoluble surface film.

The possibility that the *irfece layer might consist of PbO-PbSO4 as predicted by the Pourbaix diagram calculations was investigated. Although spectra of the sample surfaces identified tetragonal PbO, Paran spectra of the basic sulfate are not available for comparison. Infrared reflection spectra confirmed that tetragonal PbO was t', compound present. Comparison with published infrared spectra of PbO-PbSO4 (14) indicated that this compound was not present.

The oxidation currents recorded during potentiostatic exposures and potentiodynamic polarization curve measurements confirmed that lead sulfate forms more protective surface films than does PbO. In 0.1 M sulfate solutions, all of which had approximately the same conductivity and ionic strength, conditions which

caused the formation of PbO resulted in net current flow 5-10 times greater than that observed when PbSO₄ was formed. The smallest differences were noted in pH 6.3 exposures, a pH near the minimum of PbO solubility (15), but evan in those conditions oxide films allowed measurably higher current flow than sulfate films. The ability of sulfates to form an insoluble, passivating film on lead is well known.

Film Thickness: Potentiostatic exidation of vapor deposited lead samples was conducted so that the thickness of the resulting films could be measured and their spectra recorded. While films of organic compounds on silver mirrors have shown that Raman spectra of films as thin as 50 Å can be recorded (16,17) and infrared spectra of exide layers as thin as 10 Å have been reported (18), the minimum detectable film thickness varies widely with the composition of a thin film.

A lead sulfate film, measured to be 2140 _ 60 % thick, was formed by oxidation at +0.60 % in 0.1 M H_2SO_4 for fifteen minutes. The Raman spectrum in Figure 7 shows that the strong sulfate bands are clearly visible. The infrared spectrum of the same sample, shown in Figure 8, is an excellent lead sulfate spectrum. Exposure of solid lead electrodes under identical conditions formed a film which consisted of both PbSO_4 and tetragonal PbC, but the vapor deposited sample showed no trace of PbC. Presumably the thin sulfate film was not thick enough to provide the diffusion barrier necessary to allow formation of an underlying PbO layer (19).

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It is estimated that a lead sulfate film approximately one tenth of the 2140 Å thickness would still give spectra with signal to noise ratios of two or more, the ratio considered necessary for observation of a band. Films as thin as 200 Å should be identifiable by Raman and infrared spectroscopy with very little difficulty. Single spectroseter scans were used to record all spectra. Greater sensitivity to very thin films could be achieved by averaging the results of multiple scans. Signal training of more than one scan of the spectral region of interest would increase the signal to noise ratio observed and reduce the minimum diffectable thickness (20).

CONCLUSIONS

In situ Raman spectroscopy and reflection-absorption infrared spectroscopy can conclusively identify the compounds present in thin corrosion product films on metal surfaces. Using these techniques, the Pourbaix diagram for lead in 0.1 M sulfate solutions was examined and the surface species observed showed only partial agreement with predictions based on thermodynamic equilibria. Spectroscopic analysis of surface films during and after potentiostatic exposure in sulfate solutions was in excellent agreement with potentiodynamic polarization curves but the oxides and sulfates frequently formed were not those predicted in the Pourbaix diagram. The major difference was that tetragonal PbO was found experimentally in neutral and basic solutions and PbO-PbSO4, the compound predicted to be stable under such conditions, was not.

It has been shown that spectra of sample surfaces in solution and after drying are both needed to distinguish between spectral features due to solution species and those from compounds comprising insoluble surface films, just as they are both needed to determine if changes occur when samples are removed from solution. Measurement and estimation of film thicknesses have shown that the Raman and infrared techniques can identify components in films as thin as 200 Å and analyze the entirety of films as thick as one micron.

FIGURE CAPTIONS

- Figure 1. Pourbaix diagram for the Pb-H₂C-SO₄ system at 25 C for a SO₂ = $^{0.1}$.
- Figure 2. Potentiodynamic polarization curves for lead in 0.1 M sulfate solutions, scan rate 40 mV/min.
- Figure 3. Raman spectra of a) lead in 0.1 % H,SO, after 20 hours at +0.80 V, b; lead in 0.1 M H,SO, after 18 hours at +0.26 V, c) PbSG, powder?
- Figure 4. Raman spectra of a) lead surface after 19 hours at -0.16 V in 0.1 M K₂SO₄, b) PbSO₄ powder.
- Figure 5. Infrared reflection spectra obtained from lead exposed in 0.1 % sulfuric acid, pH = 0.9, at .80 % MHE for 20.5 hours. a) parallel polarization, b) perpendicular polarization.
- Figure 5. Raman spectra of lead exposed to pH 11, 0.1 M sulfate solution for 18.5 hours at -0.34 Tre-corded with the sample in solution and, after washing, in air; and the Paran spectrum of the pH 11, 0.1 M sulfate solution.
- Figure 7. Paman spectrum of a 2140 angstrom thick film of PbSO, made from a vapor deposited lead sample by exposure at 10.80 V for 15 minutes in 0.1 M HpSO. The fector at 790 and 920 cm T are grating phosts.
- Pigure 8. Infrared reflection-absorption spectra of a 2140 angstrom thick PbSO, film made from a vapor deposited lead sample. The two spectra were recorded with two different polarizations of the infrared beam. For thin films only light with its electric vector parallel to the plane of incidence interacts with the surface species.

TABLE II (cont.)

- (c) Dry sample spectrum indicated lead sulfate and orthorhombic PbO
 (d) Band at 451 cm⁻¹ abnormally intense

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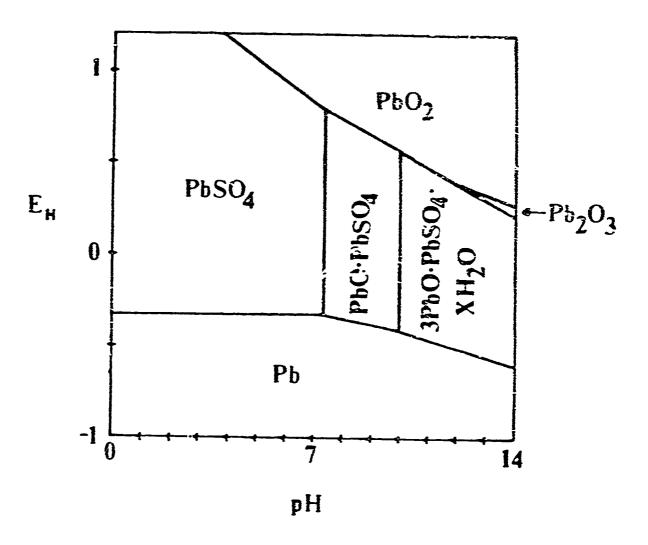


Figure 1. Pourbaix diagram for the Pb-H₂O-SO₄ system at 25° C for $a_{SO_4} = 0.1$.

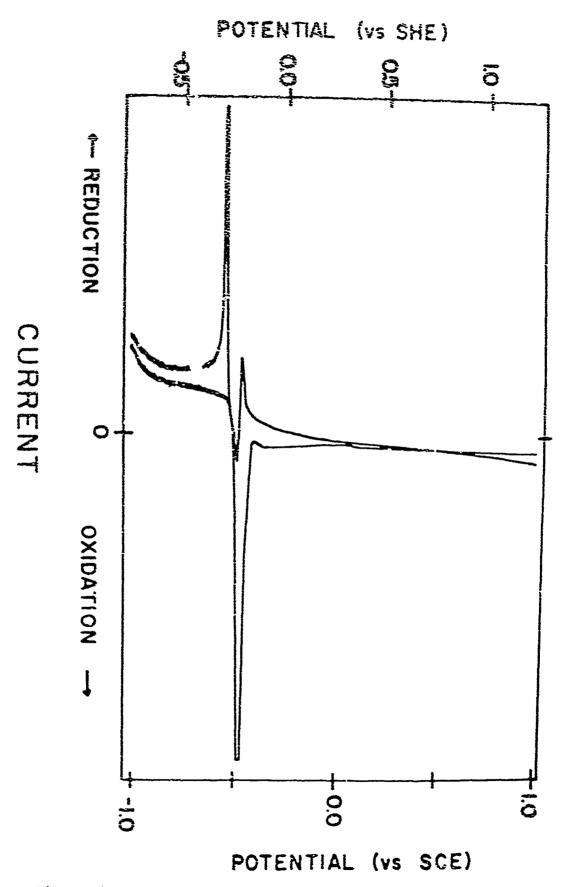


Figure 2. Potentiodynamic polarization curves for lead in 0.1 % sulfate solutions, scan rate 40 mV/min.

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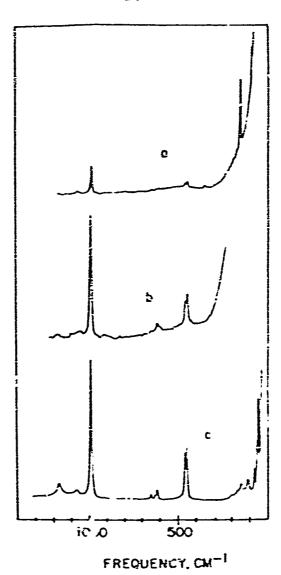


Figure 3. Raman spectra of a) lead in 0.1 M H₂SO₄ after 20 hours at +0.80, b) lead in 0.1 M H₂SO₄ after 18 hours at -0.26 T, c) PbSO₄ powder.

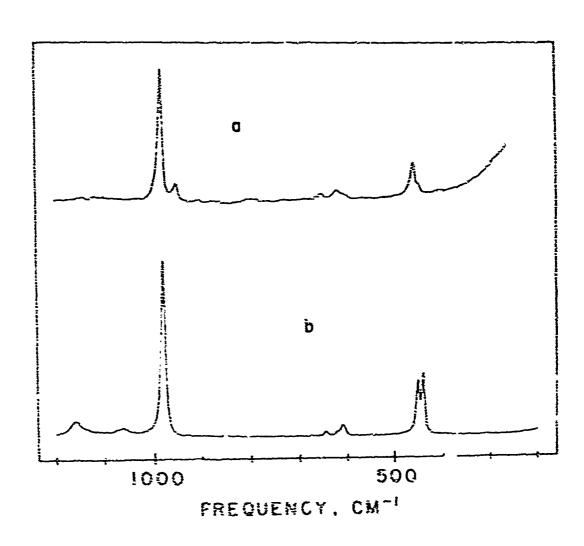


Figure 4. Raman spectra of 2) lead surface after 19 hours at -0.16 V in 0.1 K K2SO4, b) PbSO4 powder.

Figure 5. Infrared reflection spectra obtained from lead exposed in 0.1 M sulfuric acid, pH = 0.9, at .80 % NHE for 20.5 hours. a) parallel polarization, b) perpendicular polarization.

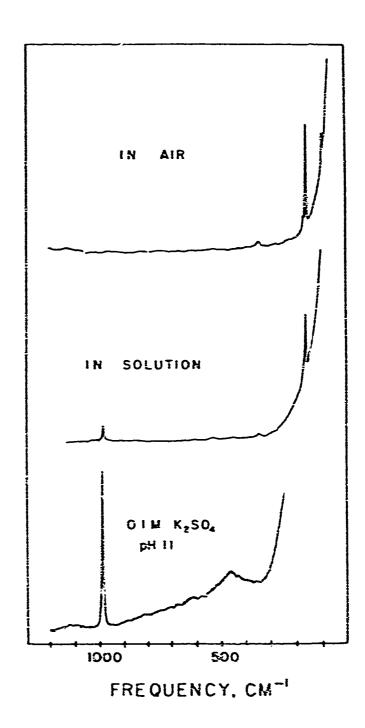


Figure 6. Raman spectra of lead exposed to pH 11, 0.1 M sulfate solution for 18.5 hours at -0.34 V recorded with the sample in solution and, after washing, in air; and the Raman spectrum of the pH 11, 0.1 M sulfate solution.

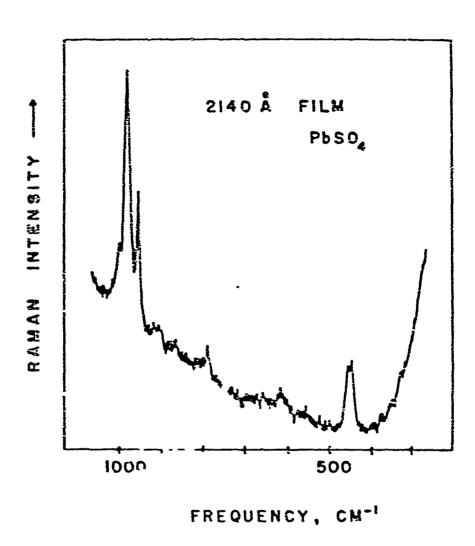


Figure 7. Raman spectrum of a 2140 angstrom thick film of PbSO, made from a vapor deposited lead sample by exposure at ±0.80 V for 15 minutes in 0.1 M H₂SO,. The features at 790 and 920 cm have grating phosts.

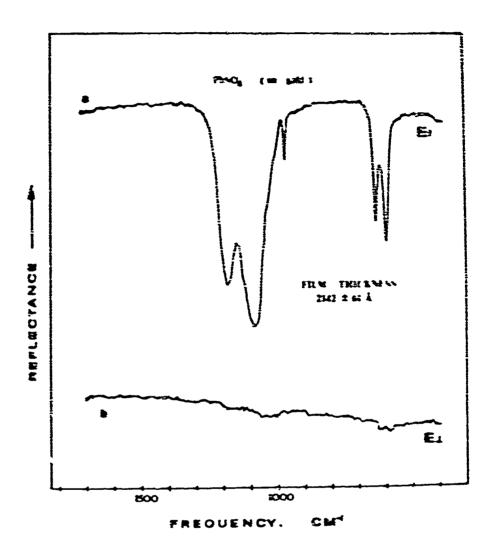


Figure 8. Infrared reflection-absorption spectra of a 2140 angstrom thick PbSO, film made from a vapor deposited lead sample. The two spectra were recorded with two different polarizations of the infrared beam. For thin films only light with its electric vector parallel to the plane of incidence interacts with the surface species.

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